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Laser Raman, infrared and far infrared spectra of 3,4,5-trimethoxybenzaldehyde

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Abstract: The infrared, far infrared and Laser Raman spectra are recorded in the region 4000-200 cm^{-1}, 500-50 cm^{-1} and 4000-100 cm^{-1} respectively. The vibrational analysis is carried out and assignments of the bands are made in terms of fundamental, combination and difference frequencies.

Keywords: Raman spectra, infrared spectra, far infrared spectra, 3,4,5-trimethoxybenzaldehyde, assignments.

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1. Introduction

The vibrational spectra of benzaldehyde, monosubstituted benzaldehydes and disubstituted benzaldehydes have been extensively investigated by many earlier workers (Garg 1954, Scrocco and Liberti 1954, Heinert and Martell 1959, Padhey and Viladker 1960, Singh *et al* 1967, Dwivedi 1968, Singh and Singh 1968, Srivastava *et al* 1968, 1969 and 1972, Singh and Sanyal 1972, Lal *et al* 1973 Green and Harrison 1976, Singh and Singh 1978, Sanyal *et al* 1981, Tariq *et al* 1982, Yadav *et al* 1982, Shashidhar *et al* 1984, Venkoji 1984, 1986). Isomeric monomethoxybenzaldehyde were reported by only few workers (Purvis 1914, Morton and Stubbs 1940, Dwivedi 1968 and Kahovec and Kohlrausch 1937). Singh and Singh (1978) have reported the infrared spectra of isomeric dimethoxybenzaldehydes. The infrared and Raman spectra of 3,4,5-trimethoxybenzaldehyde (3,4,5-TMB) were reported by Gupta *et al* (1988). But only thirteen fundamental vibrations have been observed. In the present investigation laser Raman, infrared and Fourier's transform far infrared spectra of 3,4,5-TMB are recorded and forty four fundamentals are reported. Rest of the bands are assigned in terms of combinational and difference frequencies. The depolarisation ratio of Raman bands are measured which ascertain the symmetry of the vibrations.

2. Experimental

3,4,5-Trimethoxybenzaldehyde was obtained in pure solid form from M/S K-Light Labs and used without further purification. The infrared spectrum was recorded

in the region 200-4000 cm^{-1} on PE-983 spectrophotometer using KBr pellet technique. The FT far infrared spectrum was recorded in the region 50-500 cm^{-1} on Polytech FIR 30 spectrophotometer. The polarized and depolarized Raman

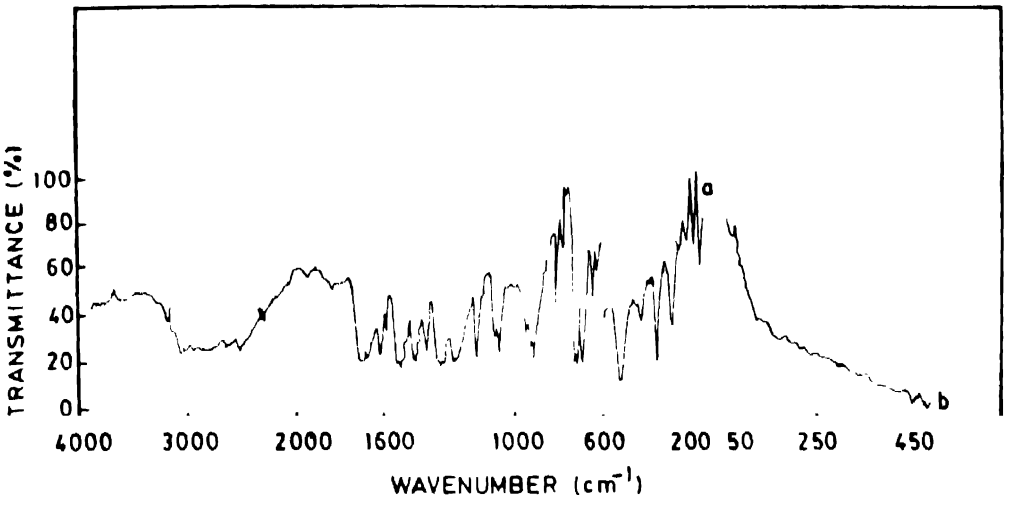

Figure 1. Infrared and far infrared spectra of 3,4,5-trimethoxybenzaldehyde: (a) infrared, (b) far infrared.

spectra were recorded, in $CHCl_3$ solution, in the region 100-4000 cm^{-1}, on Cary-82 Laser Raman spectrometer using 5145 Å line of Argon-ion laser as the

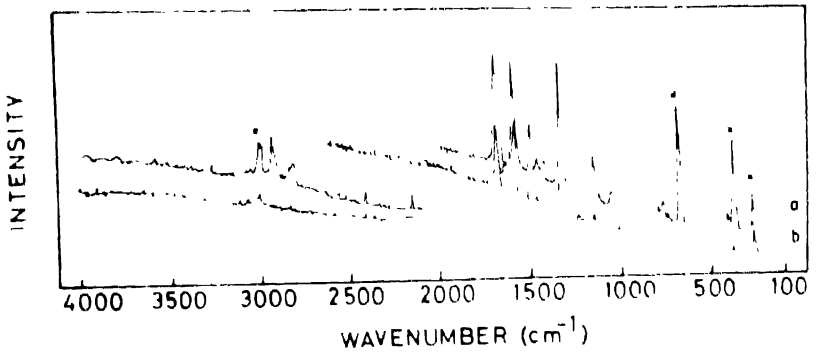

Figure 2. Raman spectra of 3,4,5-trimethoxybenzaldehyde : (a) parallel and (b) perpendicular polarization.
*Raman band of solvent.

source of excitation. The bands observed at 265, 370, 670 and 3071 cm^{-1} are due to $CHCl_3$. The traces of infared, far infrared and Raman spectra are shown in Figures 1-2.

3. Results and discussion

The molecule under present investigation is tetrasubstituted benzene. If we assume each of the substituent groups as a single mass point, it may belong to C_s point group. There will be only two types of vibrations that are a' (planar) and a'' (non-planar). For analysis of the spectra, particularly for assigning the fundamentals to different modes of vibration, assistance are taken from the studies made in the similar molecules by earlier workers and the depolarization ratio of Raman bands. Observed frequencies and probable assignments for 3,4,5-TMB are presented in Table 1.

3.1. C–X (X=substituent) stretching and bending vibration :

Earlier reports on substituted benzaldehydes (Padhey and Viladker 1960, Garg 1954, Dwivedi 1968, Singh and Singh 1978) show that C–CHO stretching frequency, which generally gives rise to strong band, appears at 1175 cm^{-1} in 3,4,5-TMB. Out of three expected C–OCH_3 stretching vibrations, only two at 928 and 944 cm^{-1} are observed in 3,4,5-TMB. These assignments are based on the studies made by Syam Sunder (1986) in 3,5-dimethoxyphenol. A very strong band appears at 525 cm^{-1} in the infrared spectrum of 3,4,5-TMB which may be assigned to C–OCH_3 in-plane bending vibration. This frequency was identified at 520 and 425 cm^{-1} in 3,4-DMB and 2,3-DMB by Singh and Singh (1978). A review of the earlier studies on substituted benzaldehydes (Venkoji 1986, Srivastava *et al* 1968 and Tariq *et al* 1982) shows that the frequency at 445 cm^{-1} appearing in the infrared and far infrared corresponds to C–CHO planar bending vibration and the frequency at 240 cm^{-1} to C–CHO out-of-plane-bending vibration.

3.2. Internal vibration of substituent groups :

C=O stretching vibration gives rise to a strong absorption in the region 1680-1815 cm^{-1}. The study of Morton and Stubbs (1940) shows that this frequency remain nearly the same on substitution of phenyl ring in place of hydrogen atom in formaldehyde. A review of earlier studies (Srivastava *et al* 1968, Sanyal *et al* 1981, Singh and Singh 1978 and Venkoji 1986) shows that the bands observed at 1685 cm^{-1} in 3,4,5-TMB may be assigned to C–O stretching vibration. The C–H stretching mode of vibration in aldehyde group is expected in the region 2730-2870 cm^{-1}. The weak band observed at 2738 cm^{-1} is assigned to this vibration in 3,4,5-TMB. The strong band at 620 cm^{-1} may be assigned to C=O out-of-plane bending vibration. Venkoji (1986) has identified this band at 625 cm^{-1} in disubstituted benzaldehyde.

One CH_3 asymmetric stretching vibration is assigned to the band observed at 2990 cm^{-1} in the molecule presently investigated. The bands observed at 2830 and 2940 cm^{-1} are assigned to CH_3 symmetric stretching vibration. CH_3

Table 1. Observed vibration frequencies (in cm^{-1}) and their probable assignment for 3,4,5-trimethoxybenzaldehyde

IR Frequencies (cm^{-1})	Laser Raman frequencies (cm^{-1})	Assignment
—	3280 w	A'' 3062+220
3078 ms	—	a' C−H stretching
3062 m	3062 m, p	a' C−H stretching
2990 w	—	a'' CH_3 asymmetric stretching
2940 w	2940 s, p	a' CH_3 symmetric stretching
2830 m	2832 ms, p	a' CH_3 symmetric stretching
2738 w	2738 w, p	a' C−H stretching in CHO group
2660 w	2660 m	A' 1620+1040
2610 w	—	A' 1680+928
2520 w	—	A' 1578+944
2500 w	—	A' 1578+928
2440 w	—	A' 1402+1040
2310 m	—	A'' 1620+692
2320 m	—	A' 1680+640
2290 w	—	A' 1515+772
2270 w	—	A'' 1578+692
2258 w	—	a'' 1343+915
2210 w	—	A'' 1515+692
2180 w	—	A' 1680+495
—	2155 m, p	A' 1456+706
2115 w	—	A' 1620+495
2075 w	—	A' 1578+495
1955 w	—	A'' 1680+272
1932 w	1932 m, p	A' 1410+525
1875 vw	—	A' 1578+297
1855 sh	—	A'' 1578+272
1840 w	—	A'' 1620+220
1820 w	—	A' 1295+525
1810 w	—	A' 1515+297
1795 w	—	A'' 1578+220
1700 sh	—	A' 1175+525
1685 b	1685 vs, p	a' C=O stretching
1674 w	—	A'' 1402+272
1648 vw	1648 w	A'' 1402+240
1620 s	1620 w	a' C−C stretching
1578 s	1580 vs, p	a' C−C stretching
1550 sh	—	A'' 915+640
1535 w	—	A'' 1295+240

Table 1 (Contd.)

IR Frequencies (cm^{-1})	Laser Raman frequencies (cm^{-1})	Assignment
1525 b	—	A' 998+525
1500 sh	1498 vs, p	a' C–C stretching
1458 b	1456 m, dp	a'' CH_3 asymmetric bending
—	1435 w, sh	A'' 915+525
1410 s	1415 m, p	a' C–C stretching
—	1380 w	A' 625+755
1360 sh	—	A'' 445+915
1335 b	1330 vs, p	a' CH_3 symmetric deformation
1290 s	1292 m	a' C–C stretching
1280 w	—	A' 803+477
1270 w	—	A'' 998+273
1175 s	1178 m, p	a' C–CHO stretching
1150 sh	—	A'' 928+220
1135 w	1135 s	a' CH_3 rocking
1117 w	—	A' 640+477
1070 vs	—	a' C–H in-plane bending
1050 sh	—	A'' 772+272
1040 s	1040 s, p	a' O–CH_3 stretching
998 m	998 m, p	a' CH_3 rocking
—	970 m, p	A' 755+220
941 s	—	a' C–OCH_3 stretching
928 m	925 w	a' C–OCH_3 stretching
915 vs	915 w	a'' C–H out-of-plane bending
803 vs	—	a' Ring breathing
775 vs	780 m, p	a' CH_3 rocking
755 ms	755 m, dp	a'' C–C out-of-plane bending
725 sh	725 w	A'' 272+455
715 vs	720 w	a'' C–H out-of-plane bending
690 vs	690 w	a'' C–C out-of-plane bending
665 sh	—	A'' 445+220
640 vs	645 w, p	a' C–C in-plane bending
620 s	625 w	a'' C=O out-of-plane bending
525 vs	525 m, p	a' C–OCH_3 in-plane bending
*495 sh 495 s	—	a' C–C in-plane bending
*485 w 490 ms	—	A'' 325+160
*465 w 465 w	—	A' 220+240

Table 1. (Contd.)

IR Frequencies (cm^{-1})	Laser Raman frequencies (cm^{-1})	Assignments
*445 s *445 w		a' C–CHO in-plane bending
*412 m *412 w	405 sh	A' 240+175
*385 vs *385 w	390 m, p	a'' C–C out-of-plane bending
325 vs	—	a' C–O–C in-plane bending
*316 sh *316 w	—	a' C–O–C in-plane bending
*300 s *300 w	300 w, p	a' C–O–C in-plane bending
272 s	—	a'' CH_3 torsion
*240 vs *230 w	240 w —	a'' C–CHO out-of-plane bending a'' CH_3 torsion
*220 vs *220 w	220 w	a'' CH_3 torsion
*180 sh	—	— 412–230
*175 w	—	a'' OCH_3 torsion
*160 w	160 m, dp	a'' OCH_3 torsion
*127 w		a'' C–OCH_3 torsion
*125 w		a'' C–CHO twisting
*120 sh		— 418–300
*75 m		— 465–385

*=frequency observed in the far infrared spectrum ; s=strong ; vs=very strong ; ms=medium strong , m=medium ; w=weak ; vw=very weak ; sh=shoulder ; p=polarized ; dp=depolarized.

asymmetric and symmetric bending vibrations are identified at 1458 and 1335 cm^{-1} in 3,4,5-TMB. The bands observed at 1135, 998 and 775 cm^{-1} are assigned to CH_3 rocking vibrations in 3,4,5-TMB. These assignments are made on the basis of comparison with studies made by earlier workers (Srivastava *et al* 1968, Scherer and Evans 1963, Singh and Singh 1978, Gupta *et al* 1983, Syam Sunder 1986, Babu *et al* 1987 and Goel *et al* 1986). The strong band at 1040 cm^{-1} may be assigned to O–CH_3 stretching vibration in 3,4,5-TMB. Singh and Singh (1978) have reported this vibration at 1035, 1025 and 1030 cm^{-1} in three isomeric dimethoxybenzaldehydes. The weak bands at 175 and 160 cm^{-1} may be assigned to OCH_3 torsion in 3,4,5-TMB. Nearly at the same frequency Sanyal *et al* (1981) have reported these vibrations. Goel *et al* (1986) have also reported these vibrations at 172 and 169 cm^{-1} in 3,4,5-trimethoxytoluene and Goel and Agarwal (1982) have assigned at 155 cm^{-1} in 4-methoxybenzonitrile. The observed bands at 272, 230 and 220 cm^{-1} are assigned to CH_3 torsional vibrations in 3,4,5-TMB. Goel *et al* (1986) have reported these vibrations at 259 and 223 cm^{-1} in 3,4,5-trimethoxytoluene. The

bands appearing at 325, 316 and 300 cm^{-1} are assigned to C–O–C in-plane bending vibration. These assignment are based on the report of Sanyal *et al* (1981) and Owen and Hester (1969) in substituted benzaldehyde and anisole respectively.

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